

THE STEREOCHEMISTRY OF COMPLEX COMPOUNDS
CONTAINING ORGANIC MOLECULES

BY

HANS BOEGH JONASSEN

B. S., Tulane University of Louisiana, 1942

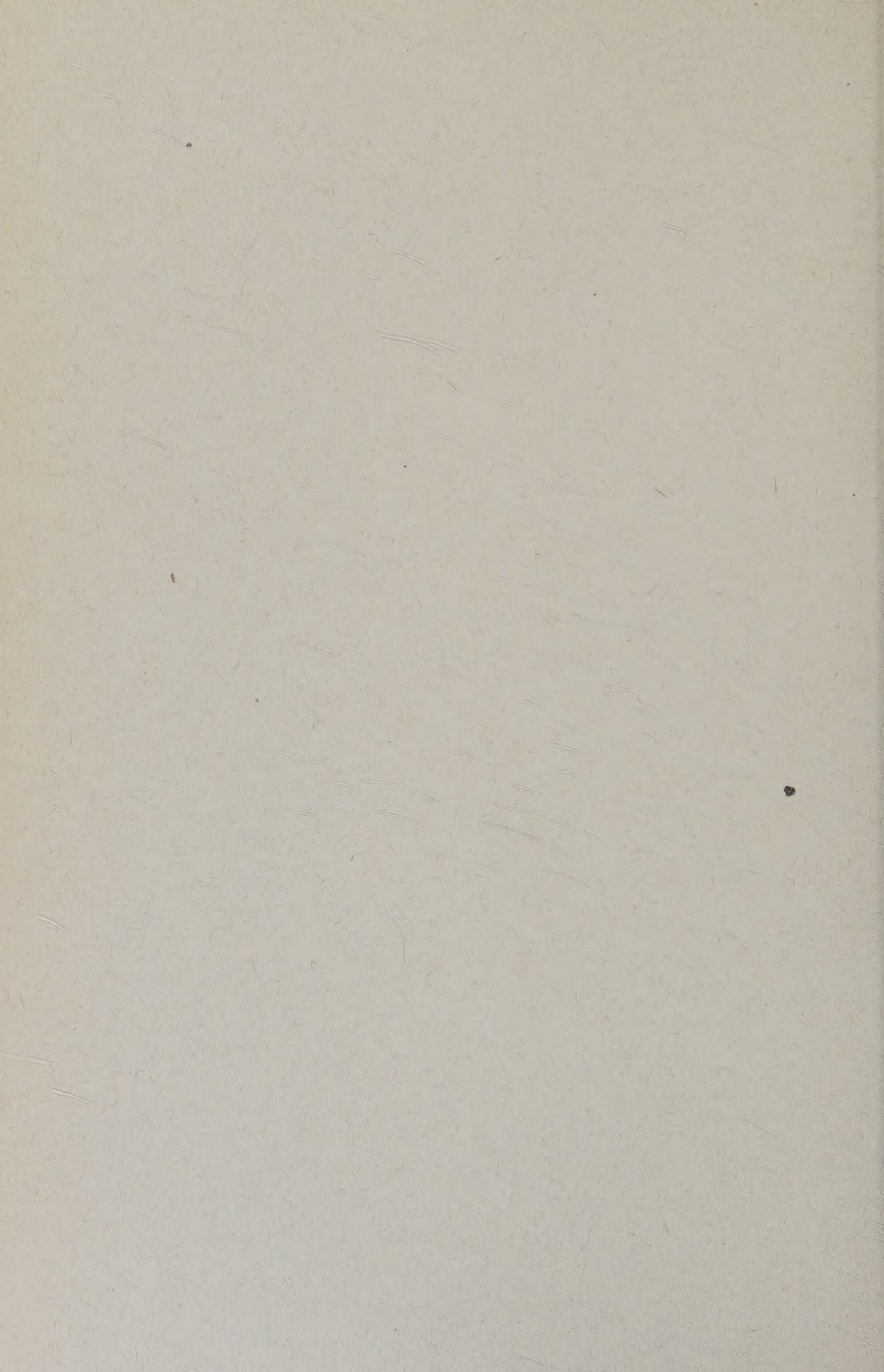
M. S., Tulane University of Louisiana, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

On the basis of the work of Jaeger¹ and Smirnoff² Bailar³ predicted in 1936 that complex inorganic compounds might be used to resolve optically active bases. Several attempts⁴ in this laboratory to bring about such resolutions met with failure.

However, the experimental evidences obtained by Huffman⁴ indicated that in the reaction of *d*-tartrato *bis*-ethylenediamino cobaltic chloride and calcium nitrite an active form of the dinitro *bis*-ethylenediamino cobaltic chloride complex was formed. Huffman also found that he never was able to obtain more than 40% of the theoretical yield; under no conditions was he able to increase this by more than about two percent. These data seem to indicate that the two forms of the *d*-tartrato react at different rates.

It was decided to study the reaction of *d*-tartrato *bis*-ethylene-diamino cobaltic bromide with ethylenediamine since in the presence of activated charcoal⁵ trisethylenediamino cobaltic bromide is formed without the necessity of heating. However, since the *bis*-ethylenediamino cobalt complexes racemize very easily whereas the *bis-levo*-propylenediamino complexes are so stable that they can be subjected to a very severe treatment without racemization, this study also includes the reaction of *bis-levo*-propylenediamino cobaltic bromide with *levo*-propylenediamine. Huffman's work with this complex also indicated that the two forms of the tartrato complex react at different rates when the dinitro-*bis-levo*-propylenediamino complex is formed.

EXPERIMENTAL

The resolved complexes used in this study were available from laboratory stock; the other complexes were made according to methods found in the literature.

Preliminary tests on resolved *tris*-ethylenediamino cobaltic bromide showed that no razemization of the active complex occurred either upon shaking with Norite (activated charcoal) or upon heating the solutions at 50° C for more than 24 hours.

Studies of the reaction of *d*-tartrato bis-ethylenediamino cobaltic bromide and 69% ethylenediamine showed that the *tris*-ethylenediamino cobaltic complex formed under these conditions was a racemic mixture. The reaction of this complex with 69% of ethylenediamine in the absence of Norite, however, produced an optically active form of the *tris*-ethylenediamino cobaltic bromotartrate. The yield was 140% of the theoretical one which showed that 40% of one form had been rearranged to the other form during the reaction. Measurements of rotation on the filtrate showed that the originally levorotatory complex increased in negative rotation as the *tris*-ethylenediamino cobaltic bromotartrate was removed.

The data obtained from the reaction of *dl*-tartrato bis-*levo*-propylenediamino cobaltic chloride and *levo* propylenediamine indicate that a partial resolution has occurred. The reaction mixture is heated at 70° C for one hour. Upon pouring this solution into ice cold methyl alcohol *tris-levo*-propylenediamino cobaltic chlorotartrate is precipitated and is removed by filtration (precipitate I). The methyl alcohol filtrate is returned to the steamcone and evaporated to dryness at 70° C. (precipitate II). The precipitates (I and II) are treated with lead nitrate after several recrystallizations and the insoluble lead tartrate is removed by filtration. It is suspended in water and saturated with hydrogen sulfide. The lead sulfide is filtered and the excess of hydrogen sulfide removed from the filtrate by boiling. The filtrate is then evaporated in a stream of air. The tartaric acid obtained from precipitate I shows a high positive rotation whereas that from precipitate II has a high negative rotation. The yields of the two fractions: Fraction I 75%, fraction II 80% of the theoretical.

DISCUSSION

The high yield in the partial resolution of *tris*-ethylenediamino cobaltic bromotartrate obtained from the reaction of *d*-tartrato

bis-ethylenediamino cobaltic bromide and ethylenediamine can be explained only if it is assumed that the following reactions take place:

- I) dextro $[\text{Coen}_2d\text{-tart}] \text{Br} \rightleftharpoons \text{levo} [\text{Coen}_2d\text{-tart}] \text{Br}$
- II) dextro $[\text{Coen}_2d\text{-tart}] \text{Br} + \text{en}^* \rightarrow \text{dextro} [\text{Coen}_3] \text{Br } d\text{-tart}$
- III) levo $[\text{Coen}_2d\text{-tart}] \text{Br} + \text{en}^* \rightarrow \text{levo} [\text{Coen}_3] \text{Br } d\text{-tart}$

Equilibrium I is displaced to the right as indicated by the negative rotation of the original bisethylenediamino complex. As ethylenediamine is added and the reaction mixture is shaken *tris*-ethylenediamino cobaltic bromotartarate is formed which has a high positive rotation. This seems to indicate reaction II is occurring predominantly in the reaction mixture. This displaces equilibrium I to the left and more of the dextro complex is formed; this change in the equilibrium concentrations will produce an increase in the negative rotation of the original complex remaining in the solution. Reaction III is also occurring in the mixture but at a much slower rate. This is shown by the fact that the rotation of the *tris*-ethylenediamino complex formed is slightly less than that of the completely resolved complex.

This is an example of resolution by the "equilibrium method" described by McKenzie and Smith⁶ and others for compounds containing asymmetric carbon atoms. This is the first time it has been used for a partial resolution of inorganic complexes.

The studies with *dl*-tartrato *bis*-*levo*-propylenediamino cobaltic chloride and *levo* propylenediamine show that the first tartrate ion removed from the complex consists mostly of the *d*-tartrate ion. Complete evaporation of the reaction mixture brings about displacement of the *l*-tartrate ion from the remainder of the complex. It is thus possible to effect a partial resolution of the two forms of tartaric acid.

*abbreviation for ethylenediamine.

SUMMARY

- 1) The first example of partial asymmetric synthesis by the "equilibrium method" is rescribed for inorganic complexes. It

involves the formation of *dextro tris*-ethylenediamino cobaltic bromide by the displacement of the *d*-tartrate ion from *d*-tartrato *bis*-ethylenediamino cobaltic halides by ethylenediamine.

2) A reaction mechanism for this resolution is proposed.

3) It is shown that it is possible to resolve racemic tartaric acid by means of the displacement of the active tartrate ion from *dl*-tartrato *bis-levo*-propylenediamino cobaltic chloride by *levo* propylenediamine.

4. It may be possible that this method of resolution may be applied to determine the absolute configuration of optically active groups which coordinate.

5. Possible application of this method for the resolution of other racemic acids or amines is discussed.

6) The advantages and disadvantages of this method over other methods of resolution is discussed.

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VITA

The writer was born in Seelze, Hannover, Germany, in 1912 and received his elementary education in Seelze. He finished the Leibniz Realgymnasium in Hannover in 1931 with the degree of Abitur. He entered Tulane University of Louisiana in 1939 and received the degree of Bachelor of Science in 1942 and the degree of Master of Science in 1944. In 1944 he entered graduate work at the University of Illinois. He has held a teaching assistantship at the University of Illinois since that time.



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